5

15

20

CLAIMS

What is claimed is:

- 1. A process of preparing ortho substituted phenylamines comprising contacting phenylhydroxylamine, optionally substituted with at least one inert substituent, with a nucleophilic reagent in the presence of a manganese oxide at a temperature between about 10° C and about 170° C and a pressure from subatmospheric to superatmospheric such that an ortho substituted phenylamine, optionally correspondingly substituted with at least one inert substituent, is predominantly formed.
- 10 2. The process of claim 1 wherein the phenylhydroxylamine is unsubstituted phenylhydroxylamine.
 - 3. The process of claim 1 wherein the phenylhydroxylamine is substituted with at least one member selected from the group consisting of C_1 - C_{10} alkyl, C_6 - C_{10} aryl, and C_6 - C_{10} alkaryl moieties.
 - 4. The process of claim 1 wherein the nucleophilic reagent is selected from the group consisting of ammonia, water, C_1 - C_{20} aliphatic alcohols, phenols, halides, and amines having the formula R'₂NH wherein each R' may independently be a hydrogen, C_1 - C_{20} aliphatic, C_4 - C_8 alicyclic, or C_6 - C_{15} aryl or alkaryl moiety.

- 5. The process of claim 1 wherein the nucleophilic reagent is an amine represented by the formula R'₂NH wherein each R' is independently a hydrogen, C₁-C₅ alkyl, or C₆-C₁₀ phenyl or alkyl-substituted phenyl moiety.
- 5 6. The process of claim 5 wherein the nucleophilic reagent is aniline.
 - 7. The process of claim 1 wherein the molar ratio of nucleophilic reagent to phenylhydroxylamine ranges from about 2 to about 100.
- A process for preparing ortho substituted phenylamines comprising contracting 10 8. phenylhydroxylamine, optionally substituted with at least one inert substituent, with a nucleophilic reagent, the molar ratio of nucleophilic reagent to phenylhydroxylamine ranging from about 2 to about 100, the contacting of the phenylhydroxylamine and nucleophilic reagent being conducted in the absence of oxygen and in the presence of a catalyst that is a 15 cryptomelane-type manganese oxide Octahedral Molecular Sieve, with a composition of $KMn_8O_{16} \cdot nH_2O$ (n = 0.5-10) in which said molecular sieve comprises MnO_6 octahedral structural units that are edge and corner shared to form a 4.6 x 4.6 tunnels as a result of 2 x 2 arrangement of octahedra, in which the potassium ions are present in the tunnels with a small amount of water and said potassium ions are ion-exchanged by H⁺ ions using nitric acid to 20 obtain the acidic form of said sieve at temperatures ranging from about 70° C to about 120° C, whereby an optionally-substituted ortho substituted phenylamine is formed in amounts equal to or greater than any concurrently formed para isomer.

- 9. The process of claim 8 wherein the phenylhydroxylamine is unsubstituted phenylhydroxylamine.
- 10. The process of claim 8 wherein the nucleophilic reagent is selected from the group consisting of ammonia, water, C_1 - C_{20} aliphatic alcohols, phenols, halides, and amines having the formula R'_2NH wherein each R' may independently be a hydrogen, C_1 - C_{20} aliphatic, C_4 - C_8 alicyclic, or C_6 - C_{15} aryl or alkaryl moiety.
- 11. The process of claim 8 wherein the nucleophilic reagent is aniline.
- 12. The process of claim 8 wherein the ortho substituted phenylamine is represented by the formula:

wherein R² is hydrogen or at least one C₁-C₁₀ alkyl moiety, and X is selected from hydroxy,

halo, C₁-C₂₀ alkoxy, phenoxy, and amino of the formula -NR'₂ wherein each R' is

independently a C₁-C₂₀ aliphatic, C₄-C₈ alicyclic, or C₆-C₁₅ aryl or alkaryl moiety.

15

10

5

- 13. The process of claim 12 wherein X is amino and the ortho substituted phenylamine is a o-phenylenediamine.
- 14. The process of claim 13 wherein theortho substituted phenylamine is o-
- 5 aminodiphenylamine represented by the formula: